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(54) **Use of propylene glycol monomethyl ether for dry cleaning**

Verwendung von Propylenglykolmonomethylether zur Trockenreinigung

Utilisation de propylène glycol monométhyl ether pour le nettoyage à sec

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(56) References cited:
FR-A- 1 544 834 **US-A- 3 701 627**

- **WORLD PATENTS INDEX LATEST** Derwent Publications Ltd., London, GB; **DATABASE WPIL**, accession no. 87-288557, week 8741; & **JP - A - 62201977 (TOYO INK MFG KK et al.) 05.09.1987**
- **JOURNAL OF RADIATION CURING** vol. 15, no. 2, April 1988, pages 3-7; **M.R. ADAMCHUK et al.: "Propylene-Based Glycol Ethers and Acetates as Substitutes for Methylene Chloride in Solvent Applications"**
- **PATENT ABSTRACTS OF JAPAN** vol. 11, no. 163 (C-424)(2610), 26 May 1987; & **JP-A-61293274 (RICOH CO LTD) 24.12.1986**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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Description

This invention relates to the use of a solvent consisting of propylene glycol monomethyl ether and water for dry cleaning. 1,1,1-Trichloroethane and perchloroethylene, which have been used in the prior art as solvents for dry cleaning, have the problem of polluting underground water, while some kinds of chlorofluorocarbons have the problem of destroying the ozone layer, and therefore there is currently a great need for rapid investigation of alternative substances.

US-A-3,701,627 discloses a process for chemical cleaning of textiles with a solvent mixture consisting essentially of a halogenated hydrocarbon, an alcohol (optionally ethyleneglycol monomethylether) and water.

JP-A-62 201977 reports a liquid for erasing a printing on a cloth, e.g., a hotel name, a hospital name etc. printed on various linens used in hospitals, hotels etc. The liquid is propyleneglycol monomethylether in combination with a reductive or oxidative bleaching agent such as hypochlorite, oxalic acid or citric acid.

The present inventor has previously investigated the dry cleaning capabilities of 81 kinds of solvents (Journal of the Japan Research Association for textile End-use 27, 8 (1986), 352 - 359), but there was no solvent which met all requirements.

A solvent for dry cleaning must meet several requirements such as detergency, handleability, safety, etc. More specifically, detergency is measured according to "solubility" and "dispersibility" of various types of soil, including oil-soluble soils such as skin fat, fat and oil, oil mist, etc.; water-soluble soils such as sweat, water-soluble foods; dirt such as sludge, dust, etc., the degree of "counter-contamination", that is, soil washed from clothing migrating back from the cleaning liquid to the clothing, and the degree of small surface tension of the solvent penetrating into the clothing and between the soils. On the other hand, "handleability" is measured by easy drying of the article to be washed, long life, easy distillation and recovery of the solvent, suitability for machines with no corrosion of metals, easy workability and management with low odor, no remaining odor on the article to be washed, etc. "Safety" is measured by the degree of collapse of form of the article to be washed, denaturation of the article to be washed such as by yellow discoloration, run-off of dye, dissolution of auxiliary items such as buttons, high ignition point and flash point, low toxicity, etc.

Propylene glycol monomethyl ether (hereinafter referred to as PM) has been known in the art as a solvent for home use (Japanese Unexamined Patent Publication No. 20400/1988), solvent for floor use (Japanese Unexamined Patent Publications Nos. 112699/1988 and 168498/1988), but not yet as a solvent for dry cleaning. The present inventor has found that PM is suitable as a solvent for dry cleaning from the standpoint of the various criteria mentioned above to accomplish the present invention.

The present invention relates to dry cleaning by using a solvent consisting of PM and water. In one embodiment, the water content is not more than 50 %, preferably 0.4 % to 25 % with respect to the total volume of the solvent for dry cleaning. It is preferable that the water content is not more than 25 %, since the shrinkage of a weft of a cotton remains by 5 %. It will be seen from the various test results described below that PM has vast possibilities.

Test example 1 (Solubility)

Water, perchloroethylene, 1,1,1-trichloroethane, CFC-113 and PM were each employed as solvent, a distillation residue of a cleaning factory was used as the oil-soluble soil and instant coffee powder as the water-soluble soil solutes. The test was conducted by adding 5 ml of the above solvent to 0.5 g of the above solute in a test tube, leaving it to stand at 30 °C for 72 hours, and thereafter examining solubility with the naked eye.

Table 1

Solute	Water	Perchloro ethylene	1,1,1-Trichloroethane	CFC-113	PM
Oil-soluble	X	○	○	○	○
Water-soluble	○	X	X	X	Δ
○: soluble, Δ: soluble, X: insoluble					

From Table 1, it can be seen that PM has both oil solubility and water solubility, and therefore is as effective on oil-soluble soils as the solvent of the prior art, and exhibits relatively better solubility for water-soluble soils, although inferior to water. In other words, while the chlorine type solvents of the prior art use soap to aid in dissolving performance for water-soluble soils, PM exhibited good detergency for water-soluble soils on its own. Also, PM has a surface tension of 27.7, which is greater than that of petroleum (18 - 19) and CFC-113 (17.3), and comparable to perchloroethylene (32.3) and 1,1,1-trichloroethane (25.6).

Test example 2 (Counter-contamination)

A solvent with little counter-contamination is good in the finishing of dry cleaning, and can clean even with a liquid containing a great deal of contamination, and the number of distillations may be economically reduced.

Counter-contamination is determined in consideration of the type of contamination (solute), the solvent and the kind of clothing, and therefore, the following test was carried out: as the water-soluble solute soy sauce (0.5 ml) and coffee (0.5 g) were used; as the dispersible solute carbon black (0.04 g) was used; as the oil-soluble solute waste oil after prolonged usage of gear oil (2 g) was used and, as the miscible solute, distillation residue of cleaning (0.04g) was employed. The test was conducted by immersing and stirring a cloth strip of 2.5 x 2.5 cm in 75 ml of a solvent containing each solute dissolved therein, and soaking it for 5 minutes. After air drying the reflectance of each cloth strip was measured by UV-200, and counter-contamination ratio was determined using the following formula.

$$\text{Counter-contamination (\%)} = \frac{\text{Reflectance of original cloth} - \text{Reflectance of cloth strip after dipping}}{\text{Reflectance of original cloth}} \times 100$$

The results are shown in Table 2.

Table 2

Solute	Clothing	Water	Perchloro- ethylene	1,1,1- Trichloro- ethane	CFC-113	PM
Soy Sauce	Cotton	2.57	*	*	*	8.75
	Wool	5.67	0.01	6.16	0.001	4.25
	Polyester	3.85	1.98	11.07	4.40	5.93
Coffee	Cotton	29.67	4.08	1.37	6.30	2.19
	Wool	22.86	21.87	5.18	32.04	2.08
	Polyester	11.95	4.56	6.39	4.29	4.87
Carbon black	Cotton	65.55	43.42	38.41	61.51	33.52
	Wool	44.31	60.90	50.53	69.98	47.08
	Polyester	53.02	42.41	42.74	50.25	64.92
Waste oil	Cotton	8.73	3.14	2.77	5.58	3.07
	Wool	*	3.29	2.38	6.94	*
	Polyester	*	2.22	2.99	2.39	*
Distillation residue	Cotton	7.16	11.18	13.05	11.05	8.09
	Wool	5.44	12.03	13.46	12.30	9.79
	Polyester	3.33	5.50	6.44	5.29	5.81

* article heavily soiled by solute

From Table 2, the following facts can be seen.

Soy sauce: Soy sauce is precipitated with a chlorine type solvent to float as a sol. The sol is hydrophilic, and therefore firmly adheres onto cotton, having a hydrophilic surface. It did not adhere to the wool or polyester, which have hydrophobic surfaces. On the other hand, since the soy sauce was completely dissolved in water and PM, no dyeing or counter-contamination was exhibited.

Coffee: In a chlorine type solvent and PM, the solute floats as solid fine particles. The particles adhered selectively with perchloroethylene and CFC-113. They did not adhere with trichloroethane and PM. On the other hand, dyeability was great with water.

Carbon black: This was not dissolved, but rather dispersed in all of the solvents, and there was no significant difference depending on the solvent.

Waste oil: This was completely dissolved in a chlorine type solvent, without counter-contamination. On the other hand, in water and PM the oil floated like a sol in the solution and since the sol is lipophilic it adhered onto the wool and polyester which have lipophilic surfaces.

Distillation residue: This is a mixture of water-soluble, dispersible and oil-soluble residues and further contains a soap for charge and therefore may be considered to approximate the conditions of practical dry cleaning. In a chlorine type solvent counter-contamination on wool and cotton was marked, while the results with water were good. With PM, the results were between those of water and chlorine type solvents.

From the results as described above, PM exhibits low counter-contamination for all kinds of contamination and clothing, and therefore can be evaluated as an excellent solvent for dry cleaning.

Test example 3 (shrinkability)

A specific feature of dry cleaning is that water absorptive fibres are prevented from form collapsing or shrinkage of washed products by swelling resulting from water washing. Shrinkage of the clothing when washed with PM or mixtures consisting of PM and water was tested.

In a cup for laundrometer in which 10 steel balls and 100 ml of solvent were placed test cloths with a thread mark of 10 x 10 cm attached at the centre of the cloth strips of 12 cm x 12 cm of cotton, hemp, wool were added sheet by sheet, soaked at normal temperature for 45 minutes, then dried by flat drying, after which the length between the thread marks was measured. The results are shown in Table 3.

Table 3

		PM 100%	PM 75% + water 25%	PM 50% + water 50%
Cotton	Warp	10.00 cm	10.00 cm	10.00 cm
	Weft	9.95	9.95	9.90
Hemp	Warp	10.00	10.00	10.00
	Weft	10.00	9.95	9.95
Wool	Warp	10.00	10.00	10.00
	Weft	9.90	9.80	9.80

As can be seen from Table 3, weft shrinkage was within 2%, but what is to be noted is that there was no great shrinkage at all even when water was added at 50%. This is due to the good hydratability of PM. In the case of 1,1,1-trichloroethane, perchloroethylene, when the water in the article to be washed mixes with the solvent, the water cannot be hydrated with the solvent and may cause the article to shrink, but PM will not give rise to such shrinkage, as shown in Table 3. However, it is preferred that the water content is not more than 25% in order that the shrinkage in any direction of the cotton does not exceed 5%.

Test example 4 (Combustibility)

The flash point of PM is 36 to 38 °C and readiness of combustion is approximately equal to that of petroleum solvents. However, the flash point of a mixture with 50% water is 62 to 64 °C, showing that elevation of the flash point can be effected by mixing with water.

Test example 5 (Readiness of drying)

In the dry cleaning process, if a long time is required for the drying of the article to be washed, work efficiency will be markedly lowered. This test was conducted by piling 4 sheets of cotton cloths of 5 x 5 cm, adding by drops 0.125

g of each solvent and measuring the vaporization rate of the solvent. The results compared the vaporization rates of the respective solvents with that of perchloroethylene (1) as shown in Table 4.

Table 4

	Perchloroethylene	1,1,1-trichloroethane	CFC-113	PM
Using cotton cloth	1	3.929	14.643	0.386
Solvent alone	1	4.444	13.667	0.244

Although PM alone is slow to vaporize, the difference is not so great when accompanied with the article to be washed such as cotton cloth. Slow vaporization rate in the case of solvent alone is desirable, because natural loss of the solvent during storage is small.

Test example 6 (Corrosiveness)

A test strip 1 x 2 cm each of iron, aluminium, and stainless steel was dipped in the solvent at room temperature for one week and then taken out and left to stand in air for 3 months for judgement of the degree of oxidation. In PM no change was observed at all for any of the test strips.

The PM of the present invention has the following advantages when used as a solvent for dry cleaning:

- (1) It is effective for washing both oil-soluble and water-soluble contaminants.
- (2) Counter-contamination is little.
- (3) No soap is required.
- (4) The life of the solvent is long.
- (5) There is no corrosion of cleaning machine, etc.
- (6) Mixing with water is possible.

Claims

1. Use of a solvent consisting of propylene glycol monomethyl ether and water for dry cleaning.
2. Use according to claim 1, wherein water is present in a concentration of 0.4 to 50 vol.% of the solvent.
3. Use according to claim 2, wherein water is present in a concentration of 25 vol.% of the solvent.
4. Process for dry cleaning comprising soaking an article to be washed with a solvent consisting of propylene glycol monomethyl ether and water and drying said article thereafter.
5. Process according to claim 4, wherein the solvent contains water in a concentration of 0.4 to 50 vol.%, preferably 0.4 to 25 vol.%, of the solvent.
6. Process according to claim 4 or 5, wherein the article is soaked with said solvent for 5 to 45 minutes.

Patentansprüche

1. Verwendung eines Lösungsmittels, welches aus Propylenglykol-Monomethyläther und Wasser besteht, zum Trockenreinigen.
2. Verwendung nach Anspruch 1, wobei das Wasser in einer Konzentration von 0,4 bis 50 vol.-% des Lösungsmittels vorliegt.
3. Verwendung nach Anspruch 2, wobei das Wasser in einer Konzentration von 25 vol.-% des Lösungsmittels vorliegt.
4. Verfahren zum Trockenreinigen, welches das Einweichen des zu reinigenden Gegenstandes mit einem Lösungsmittel umfaßt, das aus Propylenglykol-Monomethyläther und Wasser besteht, sowie das darauf folgende Trocknen des Gegenstandes.

5. Verfahren nach Anspruch 4, wobei das Lösungsmittel Wasser in einer Konzentration von 0,4 bis 50 vol.-%, vorzugsweise von 0,4 bis 25 Vol.-%, des Lösungsmittels enthält.
- 5 6. Verfahren nach Anspruch 4 oder 5, bei dem der Gegenstand 5 bis 45 Minuten lang mit dem Lösungsmittel eingeweicht wird.

Revendications

- 10 1. Utilisation d'un solvant constitué de propylène glycol monométhyl éther et d'eau, pour un nettoyage à sec.
2. Utilisation selon la revendication 1, dans laquelle l'eau est présente en une concentration allant de 0,4 à 50 % en volume du solvant.
- 15 3. Utilisation selon la revendication 2, dans laquelle est présente à une concentration de 25 % en volume du solvant.
4. Procédé de nettoyage à sec comprenant l'immersion d'un article à laver avec un solvant, constitué de propylène glycol monométhyl éther et d'eau, et séchage subséquent dudit article.
- 20 5. Procédé selon la revendication 4, dans lequel l'eau est présente en une concentration allant de 0,4 à 50 % en volume du solvant.
6. Procédé selon la revendication 4 ou 5, dans lequel l'article est immergé avec le dissolvant pendant une durée allant de 5 à 45 mn.
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